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MEASUREMENT OF ATOMIC OXYGEN IN THE
MESOSPHERE

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13. ABSTRACT <p>The oxidation rates of silver films by atomic oxygen and ozone have been examined and compared. The conductivities of the silver were measured as a function of the oxidation state. Several factors make the results of these measurements appear complex, and calibrations are necessary for atmospheric use. The apparent autocatalytic nature of the reaction and "resistance coasting" are examined in terms of a plausible mechanism. The increase in mass is amenable to direct correlation and confirms an initial rate law which is first order in the oxidation component. It was concluded that silver films are good detectors for atomic oxygen, and that ozone would not interfere with this measurement above an altitude of 38 km.</p>			

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INTRODUCTION

Recently a number of studies have been made of the reaction of atomic oxygen with thin silver films [Henderson and Schiff, 1970; Thomas and Baker, 1970]. Some of the products of this reaction are oxides of silver, which have low electrical conductivities as compared with silver. The change in conductivity of thin silver films as a method for measuring low concentrations of atomic oxygen is an intriguing possibility. Several attempts have been made to exploit this technique for atmospheric measurements in the 70-90 km region [Henderson, 1971].

In this paper we report the results of laboratory investigations of the silver-atomic oxygen reaction as well as the silver-ozone reaction. It has been found that the silver-ozone reaction is the slower of the two by several orders of magnitude. For atmospheric measurements, this means that in the daytime the silver-atomic oxygen reaction will dominate over the reaction with ozone down to a height of approximately 40-50 km. The method by which these rates were measured is described and some of the possible atmospheric applications of the technique are discussed.

MEASUREMENT SYSTEMS

In order to measure the reaction rates it was necessary to produce experimental conditions such that the rate at which the chemical species arrives at the silver surface is known. A stirred gas flow reactor was used for this purpose. In this device conditions were established so that the residence time of the gas in the reactor was long enough that uniform mixing of the reactants could be assumed, but at the same time was short enough that the chemical composition of the reactants (e.g., O in N₂) was not substantially altered. It was also important that concentration gradients should not be set up near the silver film. This condition was met by insuring that the mean free path in the reactor was long compared to the dimensions of the silver surfaces. In case of the ozone mixture, the reaction rate was so slow that the possibility

of significant concentration gradients building up in the reactor was very unlikely. Knowing the pressure of the reactor and the relative concentration of the reactants in the flow stream, calculation of the flux of particles to the surface is direct. A detailed description of the flow system and this calculation is given in Appendix A.

Given the particle flux to the surface, it remains to measure the properties of the silver film. Two such properties were measured. The first was the conductivity of the films. This is the property that is most commonly measured when the film is used as an atomic oxygen detector. Resistances have been measured over a wide range of values, nearly five orders of magnitude. Because of stability and reproducibility considerations, only the first two orders of magnitude are useful. The second measurement made was the total mass added to the silver surface during the reaction. This was done by measuring the change in frequency of an oscillating quartz crystal. As mass is added to the surface the resonant frequency of the oscillator goes down. The sensitivity of the device was such that a mass change equivalent to less than one monolayer of silver could be detected. Since the films studied were 25-100 monolayers thick, the sensitivity was sufficient to study the stoichiometry of the chemical reaction with some accuracy. The details of the resistance and mass measurements may be found in Appendix B.

Observed Phenomena

In the course of this study, which was primarily designed to determine the relative rates of reaction of atomic oxygen and ozone with silver surfaces, a number of phenomena have been observed. While they have not yet received exhaustive study, they deserve comment in this paper.

A phenomenon of some interest is the reduction of silver films which have previously been oxidized by atomic oxygen. Thomas [1970] reported the reduction of silver films by active nitrogen and Henderson [1970] by ~~active~~ hydrogen. In his work, Thomas [1970] established that the nature of silver films is changed substantially after having been oxidized and reduced (cycled). The silver becomes a matted grey color

and the film, when used as a detector, becomes more sensitive to atomic oxygen and ozone. We have found that reduction is very rapid when the oxidized film is passed quickly through a methane-oxygen flame. The current hypothesis is that this is due to OH and HO₂ present in the flame. The reduction could also be the result of heating the film since both Ag₂O and (AgO)₂ decompose above 200°C according to *Sneed, Maynard and Brasted* [1953].

A further phenomenon which has been observed is "resistance coasting," that is to say that the electrical resistance of the film continues to increase for a short time after the reaction with atomic oxygen has apparently ceased. *Henderson* [1973], however, indicates that he has not observed any significant "resistance coasting" in his experiments. *Thomas* [1971] presumes that coasting may be due to the formation of AgO on the surface followed by the migration of oxygen to the interior of the film to form Ag₂O. If this hypothesis is correct, then there should be a limit to the rate at which atomic oxygen can be delivered to the surface without causing nonlinear effects. To study these effects we have performed an experiment in a different fashion than either *Thomas* or *Henderson*. The silver-atomic oxygen reaction was turned off by suddenly admitting (within 50 ms) an atmosphere of gas. This effectively eliminates all of the atomic oxygen via three-body processes (which are enhanced by approximately 5×10^4 for $O + O_2 + M$). Figure 1 shows the results of one of these experiments, in which coasting accounts for 50% of the oxidation time and 30% of the resistance change. It was also found that this effect was more pronounced when the resistance had increased more than two orders of magnitude from its initial value. This may in part explain the differences between the observations of *Thomas* and *Henderson*.

Experimental Results

It is common in a chemical kinetic study to express the experimental results in terms of a rate law which relates a measured parameter of the reaction to the integrated or differential concentrations of the chemical species involved. Time integral concentrations (i.e.,

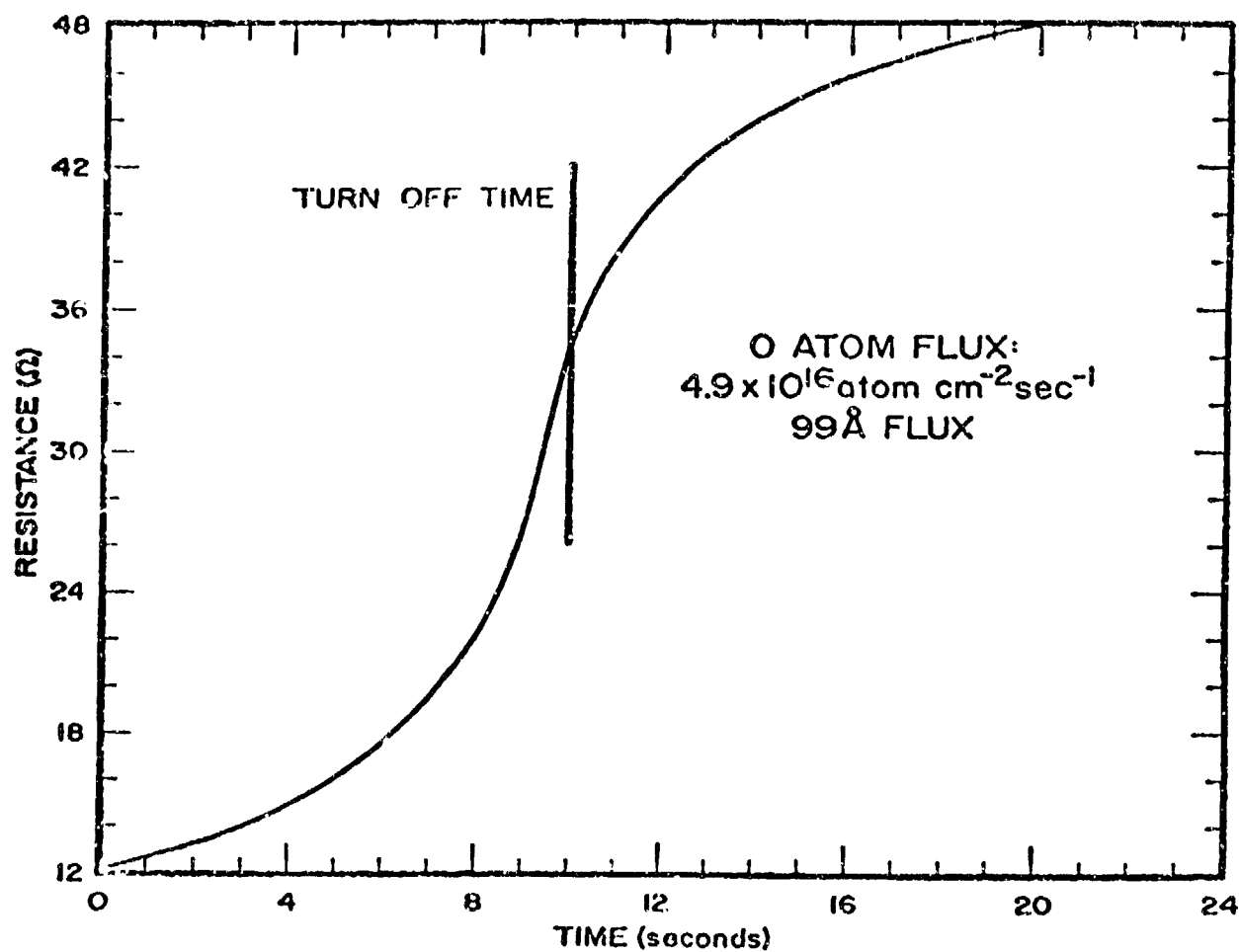


Figure 1. Resistance coating of a 99° silver film.

total number of particles to the surface of the film) and resistance are often used in studies of thin silver films used as atomic oxygen detectors. This has the disadvantage that the change in resistance may be quantitatively very complex when related to other reaction parameters. In this study therefore we have chosen to use the mass accumulation by the film when exposed to a given number of particles of atomic oxygen or ozone. A discussion of some of the reaction models proposed and their resulting rate laws may be found in Appendix C.

The mass increase of the film during oxidation by oxygen atoms follows a rate law similar to a Langmuir absorption isotherm. The initial exposure period is first order with respect to oxygen atoms as shown in Figures 2 and 3. If these data are interpreted in terms of a sticking coefficient (i.e., oxygen atoms absorbed per particle exposure), the initial coefficient for the atomic oxygen and the ozone reaction are 3.5×10^{-3} and 2.4×10^{-6} , respectively. The oxidation of silver films is accomplished 1500 times more efficiently by oxygen atoms than by ozone molecules.

CONCLUSION

We have investigated the nature of the reaction of thin silver films with atomic oxygen and ozone. We find that while the reaction with atomic oxygen is extremely rapid, the reaction with ozone by comparison is very slow. In terms of the application of these results to atmospheric measurements, this result indicates a useful altitude range of cycled thin silver film atomic oxygen detectors of from 38 km upward (see Appendix D). The method of following mass changes on a film may be more suitable for atmospheric monitoring of oxygen atoms than conductivity. The mass change is not sensitive to structural changes in the film, but only represents the ability of the film to chemisorb oxygen atoms.

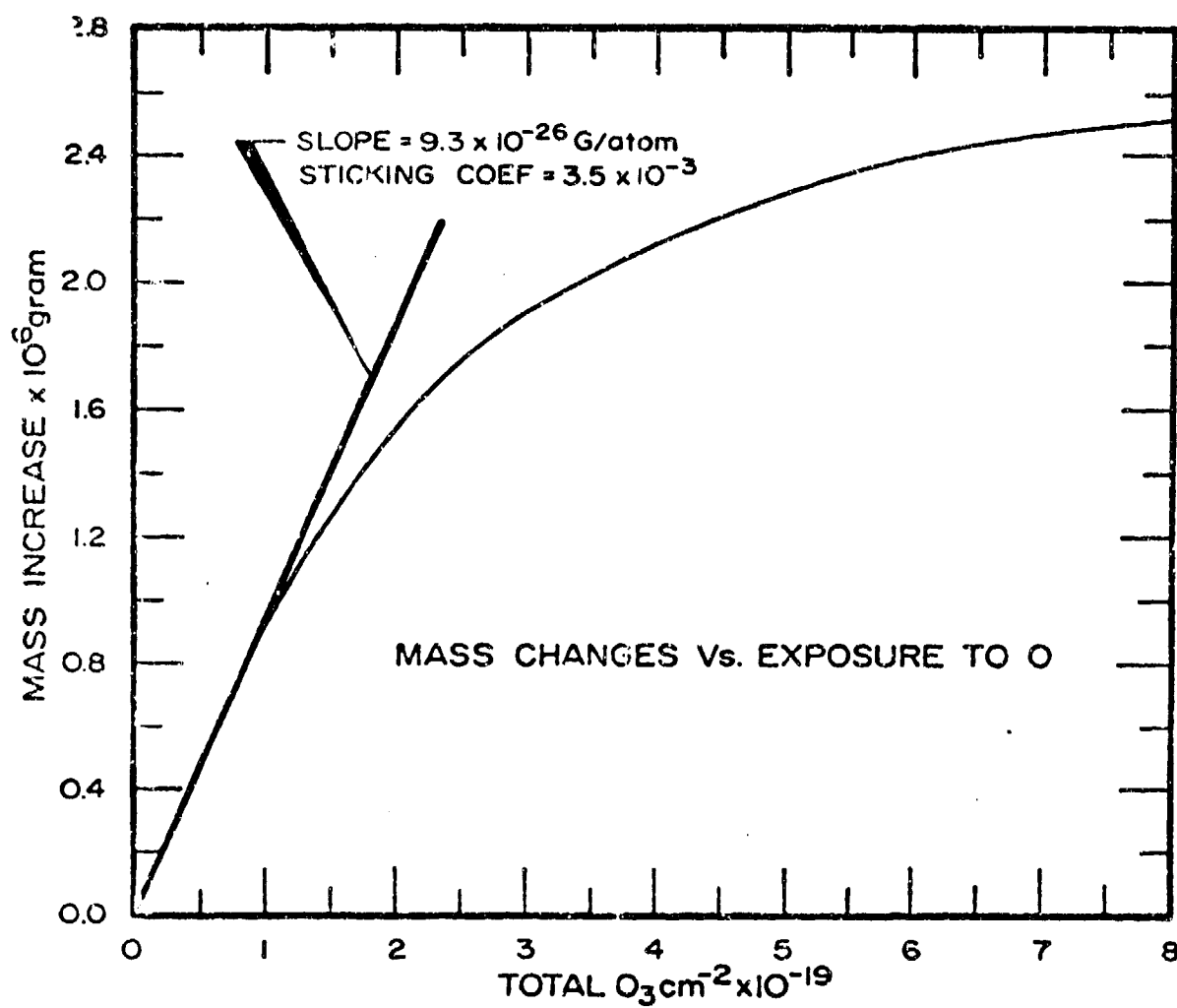


Figure 2. Mass change of a cycled 116 A film exposed to atomic oxygen.

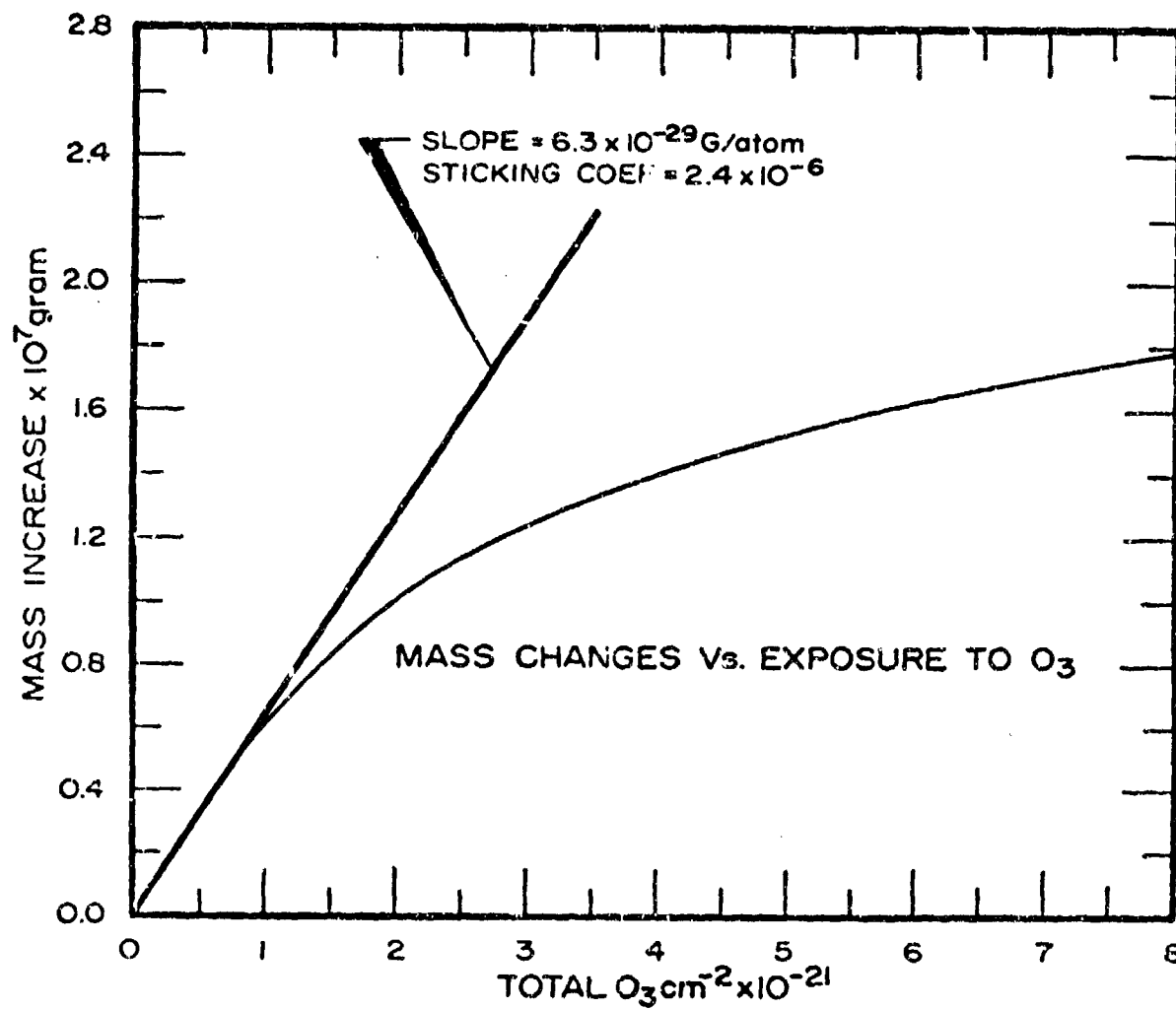


Figure 3. Mass change of a cycled 116 Å silver film exposed to ozone.

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APPENDIX A

DESCRIPTION OF O AND O₃ FLOW SYSTEMS

Calculation of Atomic Oxygen Flux to Silver Surfaces

The production of atomic oxygen in the laboratory is based upon the reaction of discharged nitrogen with nitric oxide. One of the constituents of discharged nitric oxide is atomic oxygen, which is involved in the oxygen producing reaction as follows



This reaction is commonly used because it is fast and it is exactly stoichiometric; that is, for every molecule of nitric oxide that is consumed, one atom of oxygen is produced. In the atomic oxygen apparatus (Figure A-1), the nitric oxide is discharged from a known fixed volume. Thus the rates of consumption of NO and production of O are related to the rate of change of the pressure as follows

$$\frac{dn_{\text{O,NO}}}{dt} = \frac{dp_{\text{NO}}}{dt} \frac{V_{\text{NO}}}{RT} \quad (\text{A-2})$$

The flow rate of nitrogen into the system is measured with the flowmeter and pressure transducer attached to the nitrogen tank.

Knowing the flow rates of N₂ and NO (i.e., O), the mole fraction of atomic oxygen is easily found from the ratio of these two rates. Even at its lower limit the concentration of atomic oxygen was too high to duplicate the time of oxidation expected in an atmospheric test. To remedy this the main flow stream was divided using an aperture which allowed only a fraction of the main flow stream to pass into the reaction cell. By measuring the pressure of the reaction cell and knowing the mole fraction of O, the computation of the number density of atomic oxygen and thus the flux to the surface is direct.

$$P_{\text{O}} = P_{\text{cell}} X_{\text{O}} \quad (\text{A-3})$$

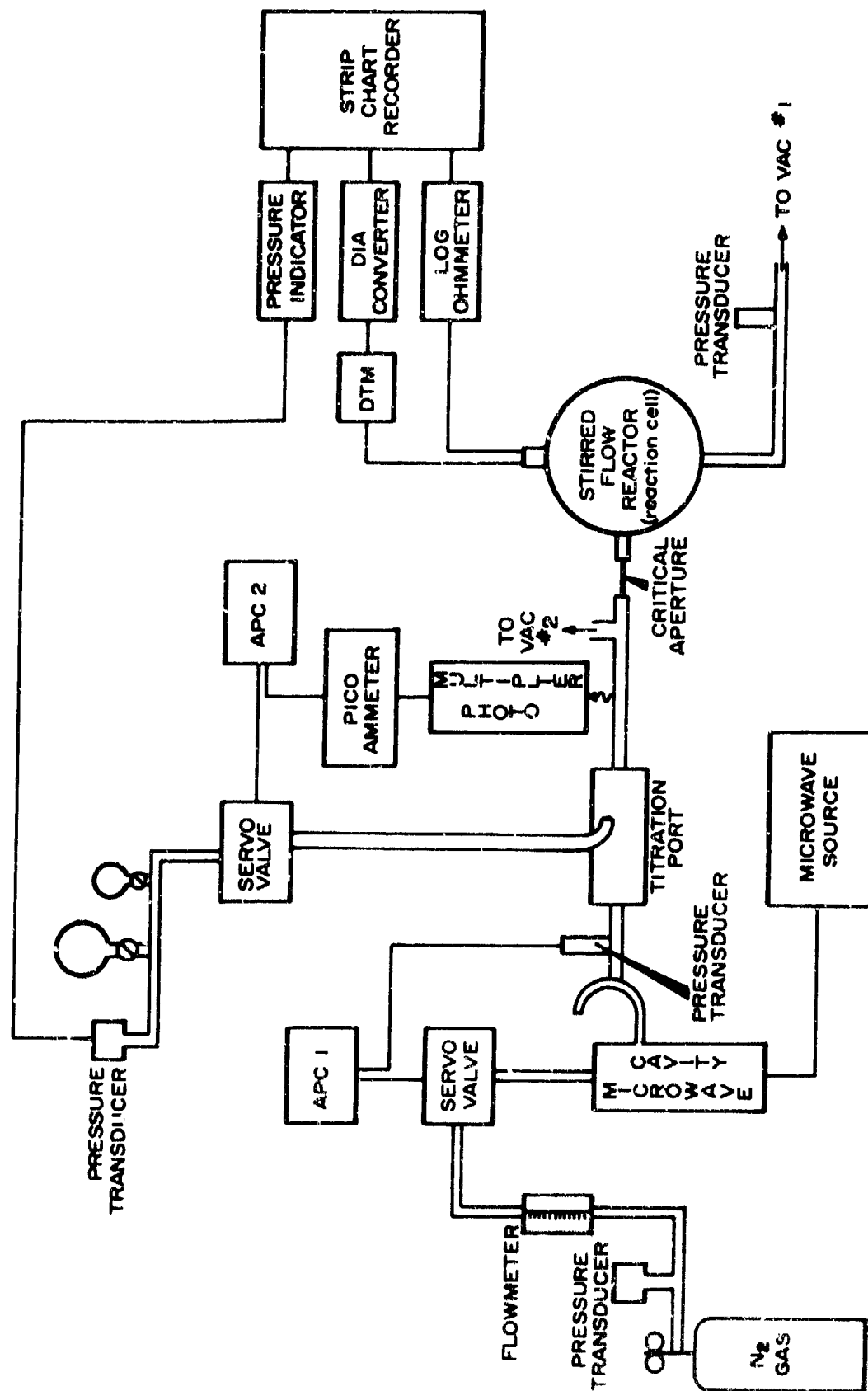


Figure A-1. Atomic oxygen apparatus.

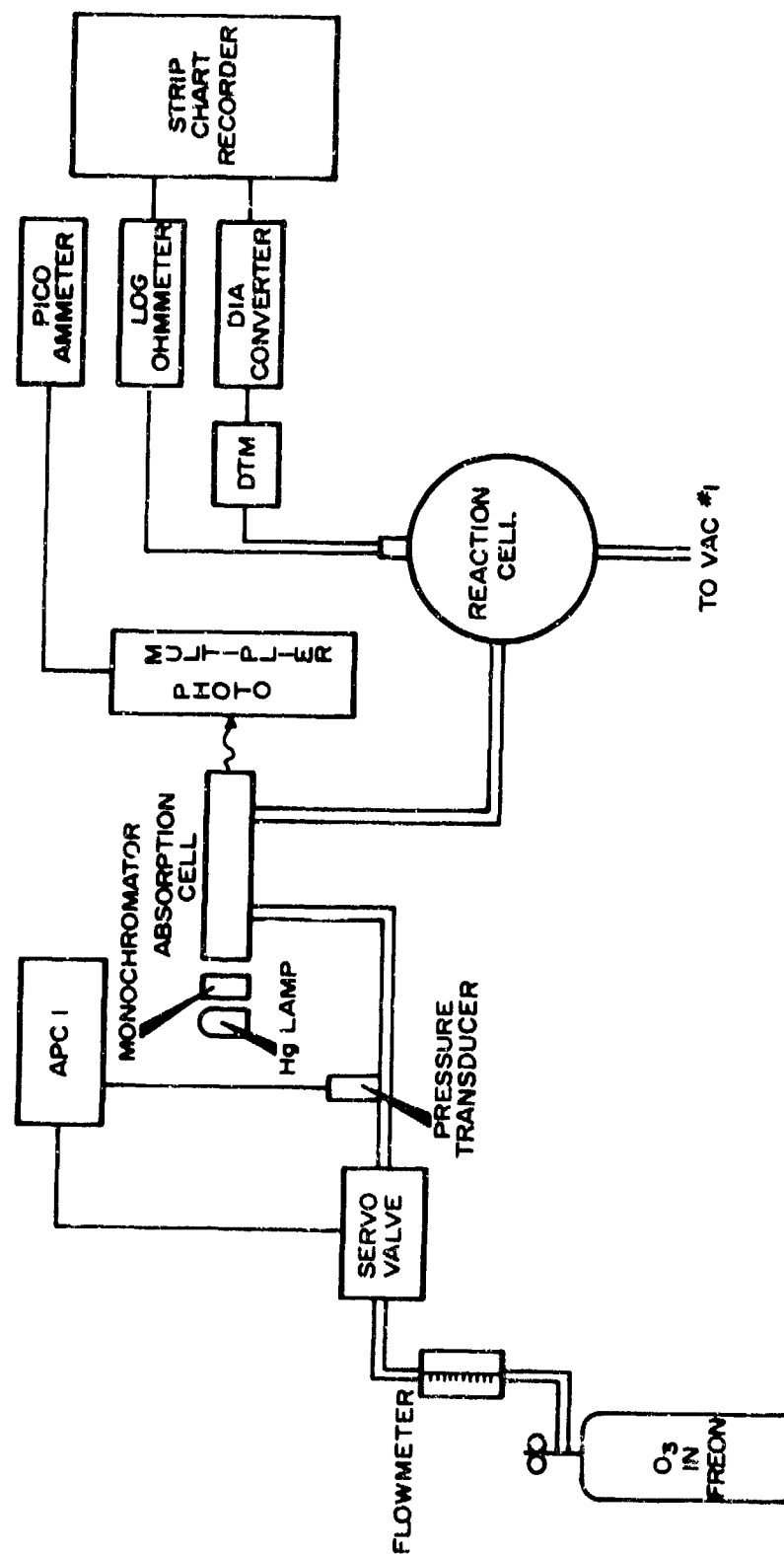


Figure A-2. Ozone apparatus.

where P_O = partial pressure of atomic oxygen in the reaction cell

P_{cell} = pressure of the cell

X_O = the mole fraction of atomic oxygen in the flow system

$$\frac{N}{V} = \frac{P_O L}{RT} \quad (A-3)$$

where $\frac{N}{V}$ = number density of atomic oxygen

R = gas constant

T = absolute temperature

$$Z = \frac{1}{4} \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{N}{V} \quad (A-4)$$

where Z = the flux of atomic oxygen to the surfaces

M = molecular weight

Functional Description of Atomic Oxygen Apparatus

A pressure transducer in combination with the flowmeter provides a means of measuring the flow rate of nitrogen into the system. Automatic pressure controller 1 (APC1), a servovalve and pressure transducer, maintains a constant pressure in the flow manifold. The microwave source and cavity discharges the nitrogen in the flow stream to produce atomic nitrogen used in the O-producing reaction. When nitric oxide is added to reaction (A-1) in slight excess of the stoichiometric amount, visible light is emitted from excited NO_2 . The brightness of this light is used to control the rate at which NO is added to the atomic oxygen-producing reaction. This control action is provided by the photomultiplier and the picoammeter, which supply the electrical signal necessary for APC2 to operate the servovalve, which in turn allows nitric oxide to flow from a known, fixed volume to the flow stream via the gas titration port. The pressure in the fixed volume is recorded on a strip chart recorder. The mass added to the silver film is measured by a commercially available digital thickness monitor (DTM) as described in Appendix B. In order to be recorded simultaneously with the other data, the signal from the DTM was converted from digital to analog. The resistance of the silver film was measured using a log ohmmeter which had an analog signal output proportional to the logarithm of the film resistance.

Calculation of Ozone Flux to the Silver Surfaces

The calculation of ozone flux to the silver surfaces also made use of equation (A-5). The number density and partial pressure of ozone were computed using the same procedure that was used for the atomic oxygen calculations. The mol. fraction, however, was found spectroscopically rather than from the flow rate and was computed knowing the pressure of the spectrophotometer cell and the absorption of the ozone at 2450 Å.

$$X_{O_3} = \frac{\log \left(\frac{I_0}{I} \right)}{c \cdot \chi \cdot P_{\text{cell}}} \quad (\text{A-5})$$

where X_{O_3} = mole fraction of ozone

I_0 = intensity of the light transmitted through the cell without O_3 present

I = intensity of the light transmitted through the cell with O_3 present

P_{cell} = pressure of the spectrophotometer cell

c = extinction coefficient for ozone at 2450 Å; i.e., 138 atm cm^{-1}

χ = the length of the spectrophotometer cell

Functional Description of Ozone Apparatus

The flow of the ozone-freon gas was determined with the flow meter, and the flow manifold was kept at a constant pressure using APC1 in combination with a servovalve and pressure transducer. The log ohmmeter and DTM served the same purpose as in the atomic oxygen flow system.

APPENDIX B

MASS AND RESISTANCE MEASUREMENTS

Mass Measurement

The mass measurements were made using a commercially available digital thickness monitor (DTM). As mass builds up on the face of an AT-cut quartz crystal, the resonant frequency changes according to the equation

$$dm = \frac{NPA}{fS} dx \quad (B-1)$$

where $N = 1670 \text{ kHz-mm}$

$P =$ density of quartz

$A =$ crystal area

$f =$ reference frequency (7.6025 MHz)

$S =$ instrument scale factor (2×10^6)

$dm =$ change in mass

$dx =$ change in instrument count

From equation (B-1) it was determined that this particular device had a sensitivity of $1.9 \times 10^{-8} \text{ g count}^{-1}$. The DTM was very stable and a change of more than one count was taken as significant data.

Resistance Measurement

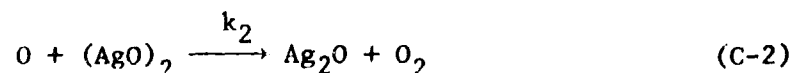
The electrical resistance of the silver film was measured using a device which had a voltage output which was the logarithm of the resistance at the input. This transfer function was generated by a voltage divider which made use of the logarithmic forward characteristics of a diode. Since the forward characteristics of a diode are temperature dependent, it was controlled at a constant temperature. The voltage at the division point was buffered with a high impedance amplifier so that it could be read with a strip chart recorder.

APPENDIX C

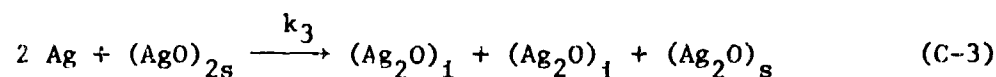
CHEMICAL MODELS AND RESULTING RATE LAWS

Thomas-Baker Model

Several chemical models have been proposed for the oxidation of silver films by atomic oxygen. Perhaps the most detailed one is proposed by *Thomas and Baker* [1971] and is developed in equations (C-1) to (C-8). They use as a basis the two competing reactions proposed by *Myerson* [1967]



Equation (C-1) accounts for oxidation of and (C-2) for recombination on a partially oxidized silver surface. Further, they propose that the silver below the film surface is oxidized by an oxygen transfer reaction (C-3) with $(AgO)_2$ acting as an intermediate



where (i) indicates "interior" and (s) indicates "surfaces." The rate of oxidation of the film from equation (C-3) is

$$R = \frac{d[(Ag_2O)_i]}{dt} = k_3 [(Ag)_i]^2 [(AgO)_{2s}] \quad (C-4)$$

Using the steady state approximation for $(AgO)_2$ and considering the densities at the surface, equations (C-5) and (C-6) result.

$$\frac{Ag_2O}{(AgO)_2} = \frac{1}{k_1} \left[k_2 + \frac{k_3 [Ag]^2}{[O]} \right] \quad (C-5)$$

$$[(AgO)_2] + [Ag_2O] = C \quad (C-6)$$

where C is a constant. Combining equations (C-5) and (C-6) and eliminating $[Ag_2O]$ the rate becomes

$$R = \frac{C k_1 k_3 [Ag]^2 [O]}{k_1 [O] + k_2 [O] + k_3 [Ag]^2} \quad (C-7)$$

They conclude that if $[O] \ll k_3 [Ag]^2 / (k_1 + k_2)$ as is the case at early times in the oxidation, then the rate is proportional to the atomic oxygen flux $[O]$.

$$R = C k_1 [O] \quad (C-8)$$

Consequences of the Thomas-Baker Model

The Thomas-Baker model, by use of equation (C-3), predicts that silver should continue to be oxidized even after the atomic oxygen flux has stopped (referred to as coasting) provided that k_3 is relatively small. This causes O transport to become pronounced as the oxide layer builds up, decreasing the effective magnitude of k_3 . As mentioned in this paper, coasting has been observed and does indeed become more pronounced as the oxide layer becomes thicker, in agreement with the model. Also the initial mass build up on the film has been observed to be proportional to the total number of oxygen atoms to which it has been exposed as predicted by the Thomas-Baker model.

The Thomas-Baker model presumes several aspects (listed below) which may introduce significant errors.

1. The model does not account for the initial oxidation of the silver surface but assumes it to be uniformly oxidized to Ag_2O (see reaction (C-1)) before reaction (C-1), (C-2), and (C-3) proceed. If this assumption is not valid then the initial $Ag + O$ reaction must be considered as competing with reactions (C-1) and (C-2). Myerson [1967] indicated that Ag_2O rather than $(AgO)_2$ is formed when silver is first exposed to atomic oxygen.

2. The model assumes $[Ag_2O] + [(AgO)_2]$ to be a constant C . As the underlying silver becomes oxidized via reaction (C-3), the region active in O transport increases in depth and C must become larger. This is not provided for in the model.

3. The model also assumes a film which is fairly compact so that the underlying silver is oxidizable only by transport of oxygen from the surface layer. If the film is porous then underlying silver may be oxidized without requiring the formation of the intermediate compound $(AgO)_2$. If this is the case, then the oxidation rate law would also be linear initially, as is observed. However, little coasting would be detected, as observed by *Henderson*. It would be well to mention here that coasting could also be due to extensive absorption of atomic oxygen. The mechanism of coasting could be tested by observing the mass change of a film sufficiently thick that a substantial amount of silver was not in direct contact with the oxidizing atmosphere. Under these conditions only transport of O should be responsible for extensive oxidation as in reaction (C-3).

APPENDIX D

APPLICATION TO AERONOMY

One of the motivations for studying the response of thin silver films to active species stems from the fact that such films are nearly specific to atomic oxygen. They can, therefore, be used to measure atomic oxygen height profiles in the region below 100 km where the use of mass spectrometers has been extremely difficult. The specie in this part of the atmosphere which is most likely to compete with atomic oxygen in the reaction with the silver films is ozone. In this study it was found that exposure to ozone caused a cycled detector (i.e., one which had been oxidized then reduced) to gain mass at a rate 6×10^{-4} as fast as a similar one exposed to atomic oxygen. If the resistance change vs. mass added is the same for the ozone and atomic oxygen reaction, then atomic oxygen detectors should be usable to altitudes at which $[O]/[O_3]$ is approximately 6×10^{-4} . (Reference to atmospheric models indicate that this is reached at about 38 km for daytime conditions.) At night, however, the atomic oxygen recombines and the $[O]/[O_3]$ ratio approaches zero below 70 km. This suggests that silver film atomic oxygen detectors are more usable during daylight hours.

The daytime ratio of $[O]/[O_3]$ is a very important parameter in the study of mesospheric chemistry. It appears that a silver film detector aboard a parachute-borne payload might represent a viable measuring technique. At altitudes near 50 km, however, the OH radical reaches significant concentrations and its reactivity toward silver oxides may be such that substantial errors would be introduced into the measurement of atomic oxygen. Plans are being made to determine this sensitivity to OH with the idea that if they are sufficiently sensitive, oxidized silver films could be used as OH detectors.